Graphene-based Systems for Energy Storage

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- Every exploration plan calls for a sustainable exploration architecture.

- Living in space requires supplies of energy, air, water, and food
- We can initially supply our habitat with those commodities, but we must have systems able to regenerate some of those essential items.

Current Spacecraft Batteries

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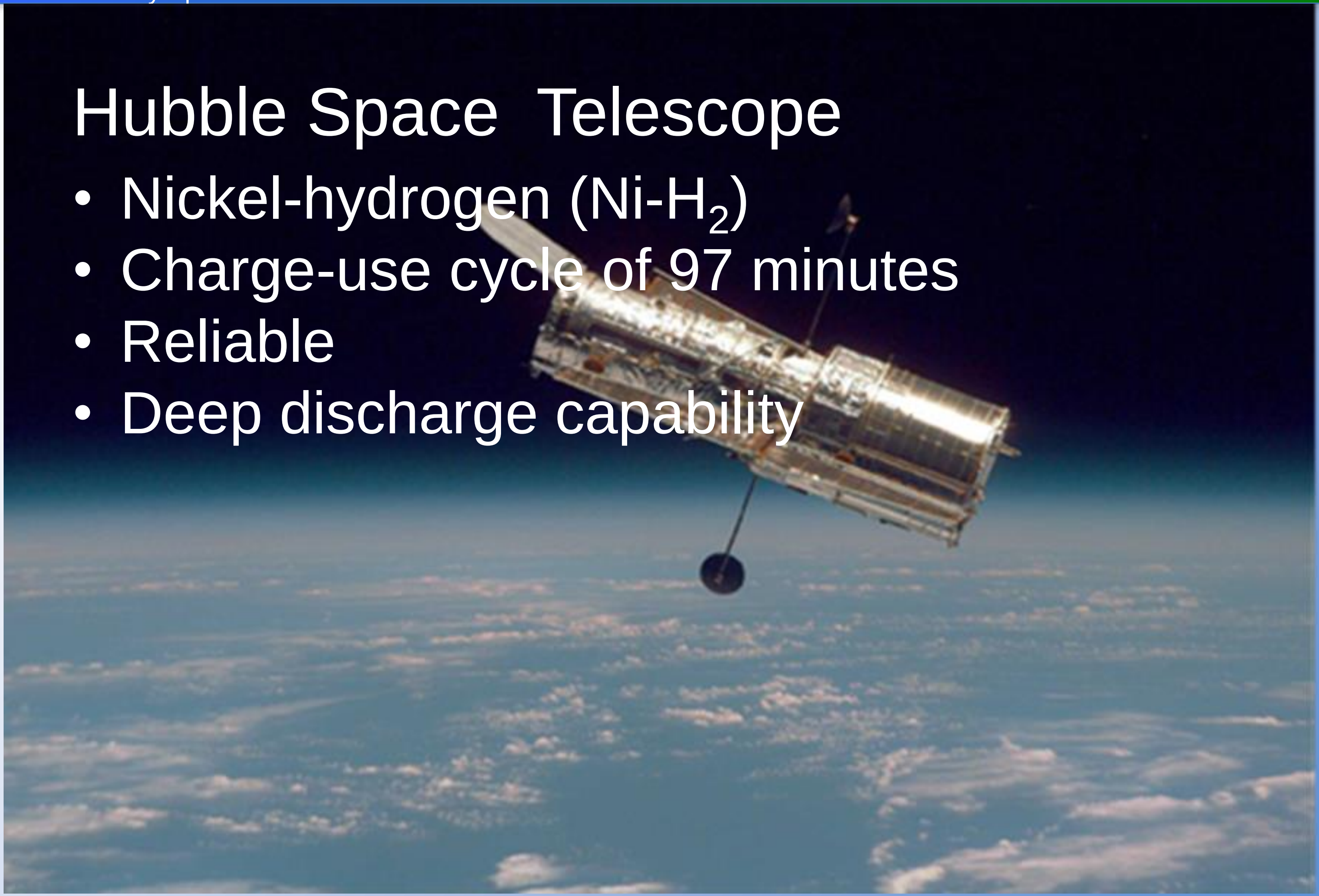


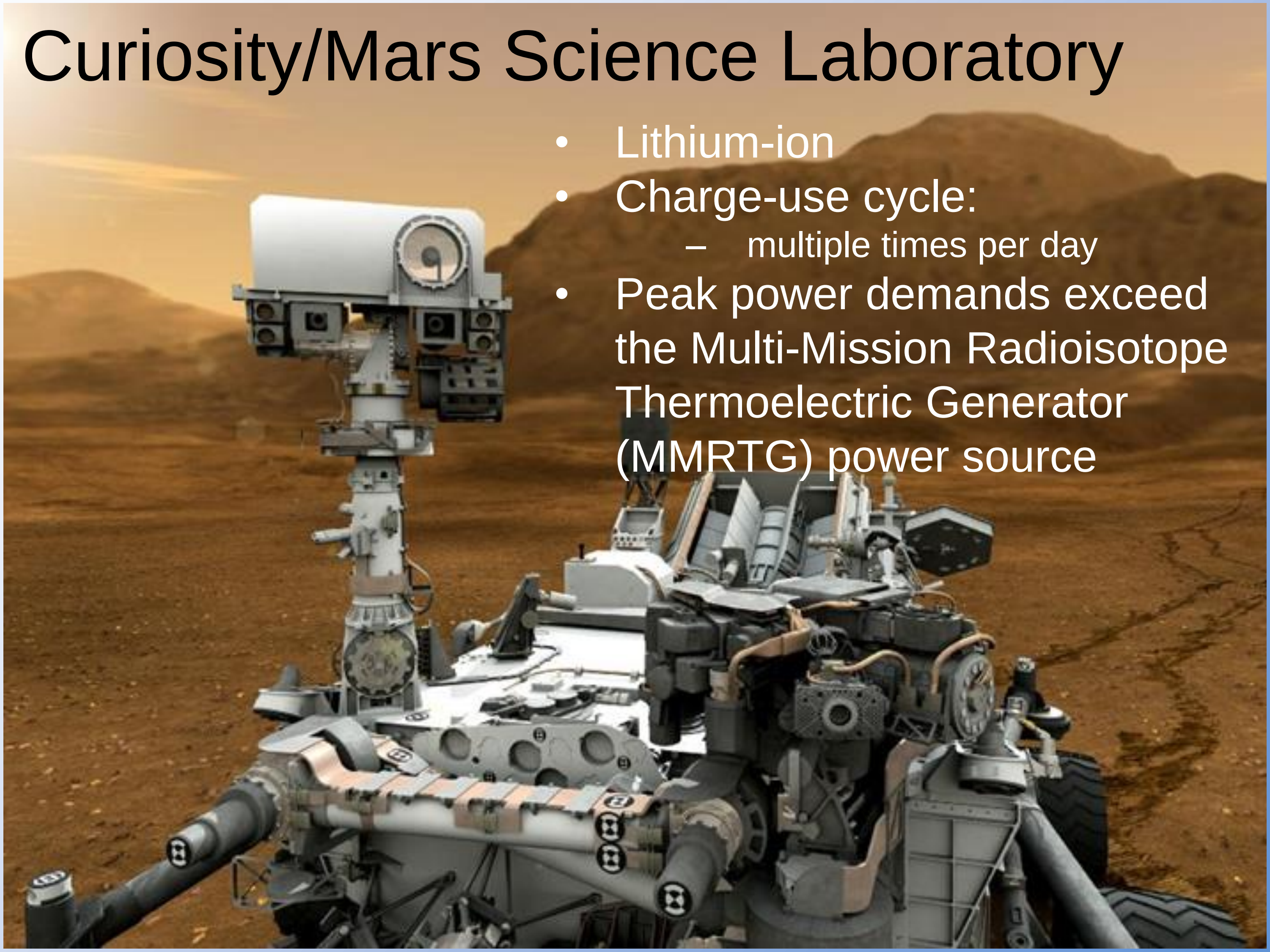
Hubble Space Telescope

- Nickel-hydrogen (Ni-H_2)
- Charge-use cycle of 97 minutes
- Reliable
- Deep discharge capability

Evolving Technology

Curiosity/Mars Science Laboratory

- Lithium-ion
- Charge-use cycle:
  - multiple times per day
- Peak power demands exceed the Multi-Mission Radioisotope Thermoelectric Generator (MMRTG) power source



Mars Battery Requirements

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The MSL rover uses a Multi-Mission Radioisotope Thermoelectric Generator (MMRTG). To augment the MMRTG, a rechargeable Li-ion battery is being used.

Li-ion Battery Functions to Augment MMRTG throughout Mission

- Provide power during launch
- Assist thermal batteries during entry, descent, and landing (EDL)
- Support power loads on the Mars surface that exceed the Multi-Mission Radioisotope Thermoelectric Generator (MMRTG)

Mission Requirements for the Li-ion Battery

- Ability to be stored for 6-12 months
- Provide 920 Wh with $V > 25$ V, $i_{max} = 22$ A during launch
- Survive cruise phase at 50-75% State of charge (SOG), -20ºC $\leq T \leq$ +40ºC
- Support backup power: 30A pulses at 100% SOC
- Support EDL loads: 25A pulses
- Augment MMRTG during surface operations for at least 670 sols

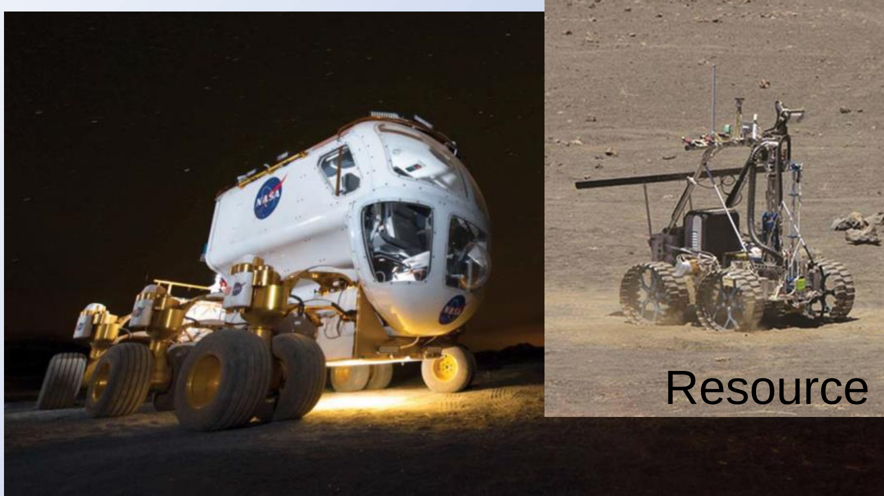
Operational Requirements on the Mars Surface

- Charge and discharge at -20ºC $\leq T \leq$ +30ºC
- Operate for >2000 cycles with depth-of-charge $\leq$ 45%
- Operating voltage $\geq$ 25 V

Multi-Mission Radioisotope Thermoelectric Generator

Potential Future Missions

- Future missions will require higher energy and power density to enable:
  - High power robotics
  - In-Situ Resource Utilization (ISRU)
  - Exploration



Space Exploration Vehicle (SEV)

Resource Prospector

RASSOR

Future Power Requirements

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- Higher specific energy rechargeables
  - long life (500 Wh/kg, 5000 cycles)
  - low temperature (200 Wh/kg, -100° C)
  - High temperature (450° C)
- High specific energy primary storage
  - low temperature (1000 Wh/kg, -160° C)
  - high temperature (1000 Wh/kg, 450° C)
- Green battery materials and processes
- Advanced electronics to implement optimized charge methodologies to enhance life and safety.

New Materials

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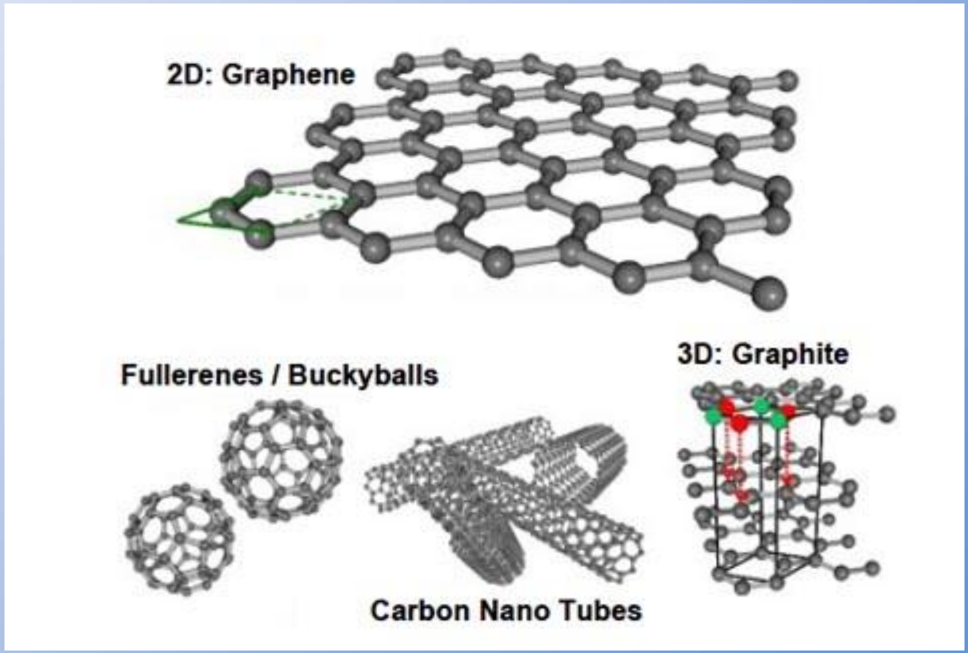
- New nanomaterials offer possibilities for new technologies
- Graphene, a one-atom-thick, two-dimensional array of carbon atoms is one of the most promising materials



What is Graphene?

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- **Graphene is a revolutionary new allotrope of carbon (a single atomic layer of graphite) with extraordinary properties:**
  - ***Surface area*: 2630 m^2/g**
  - ***Electrical conductivity*: $10^6\ \Omega^{-1}cm^{-1}$ (Cu: $0.6 \times 10^6\ \Omega^{-1}cm^{-1}$)**

    π-electrons act like photons – mobility is determined by graphene quality
  - ***Thermal conductivity*: 5000 $Wm^{-1}K^{-1}$ (Cu: 401 $Wm^{-1}K^{-1}$)**
  - **Strongest material ever discovered: Tensile strength ~ 130 GPa (steel ~0.4 GPa)**
  - **"Graphene is complicated and expensive to make in large sheets" *Nature*, Nov. 20, 2013**

The Innovation

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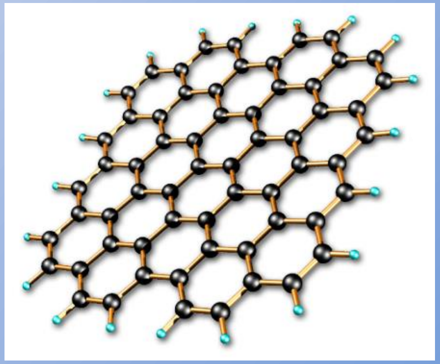
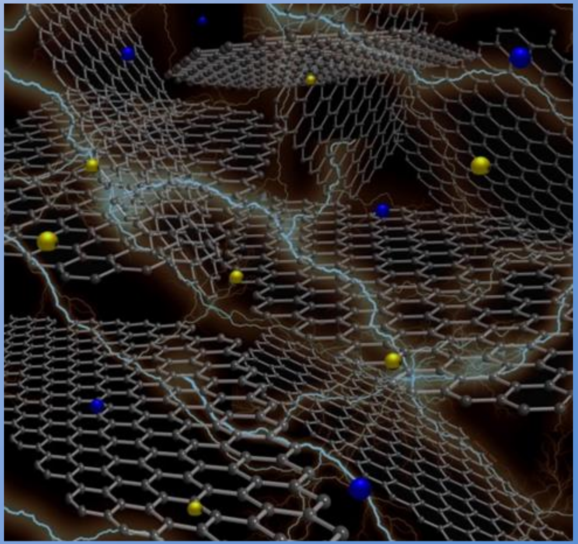
- Develop a graphene-based ultracapacitor prototype that is flexible, thin, lightweight, durable, low cost, and safe and that will demonstrate the feasibility for use in aircraft
- These graphene-based devices store charge on graphene sheets and take advantage of the large accessible surface area of graphene (2,600 m^2/g) to increase the electrical energy that can be stored.
- The proposed devices should have the electrical storage capacity of thin-film-ion batteries but with much shorter charge/discharge cycle times as well as longer lives
- The proposed devices will be carbon-based and so will not have the same issues with flammability or toxicity as the standard lithium-based storage cells.





Theoretical surface area = 2630 m^2/g

Laser Scribed Graphene

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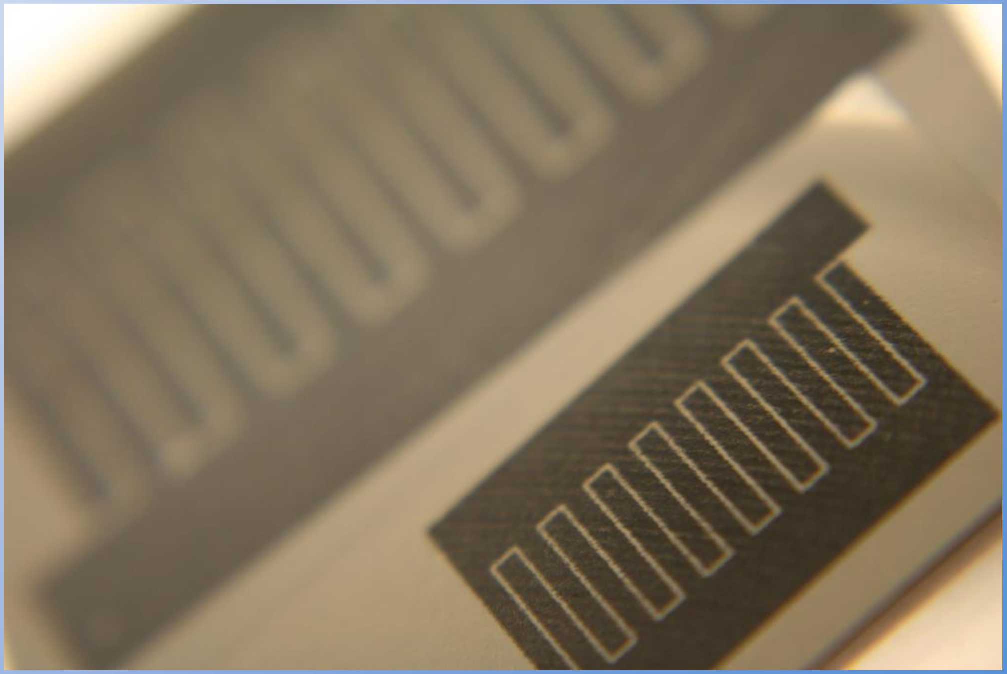
- UCLA and NASA: Use of laser to reduce Graphene Oxide
  - Exfoliates layers while removing oxygen
  - Result is a large surface of area of graphene crystals



Picture credit: Rachel E Cox, NASA

LaserScribe: Graphene in a DVD

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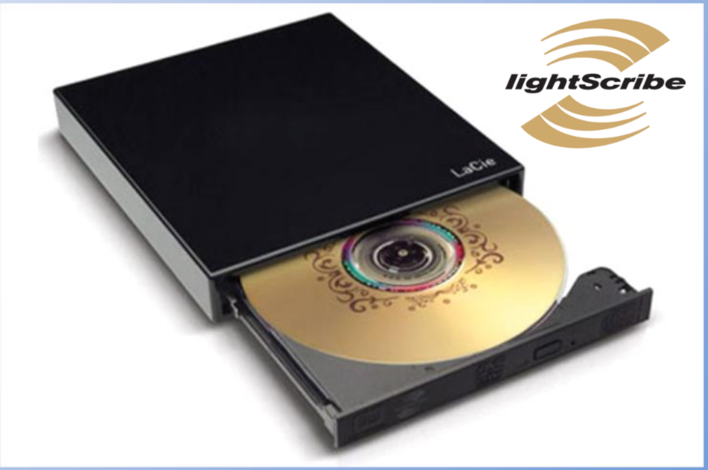

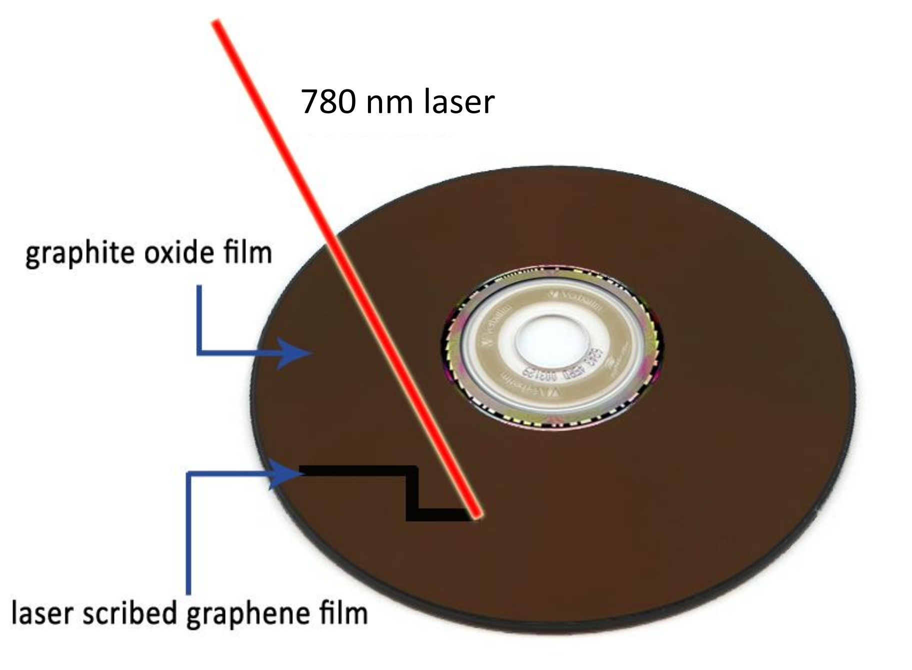

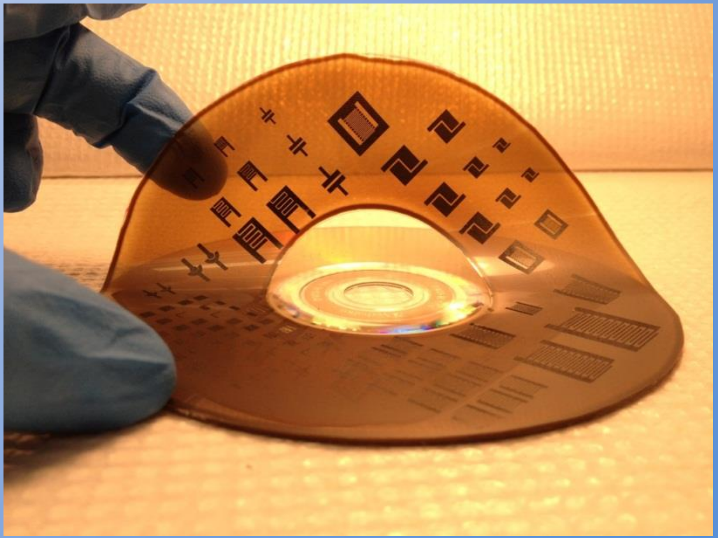

Our Results: XPS Analysis

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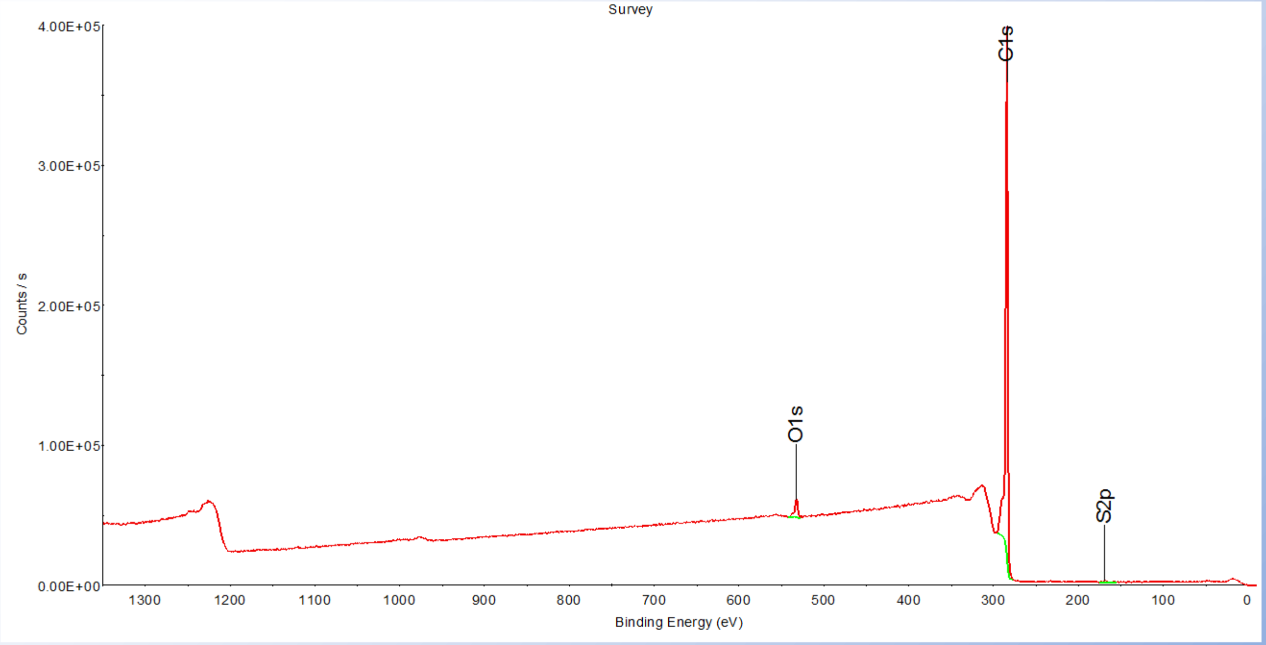
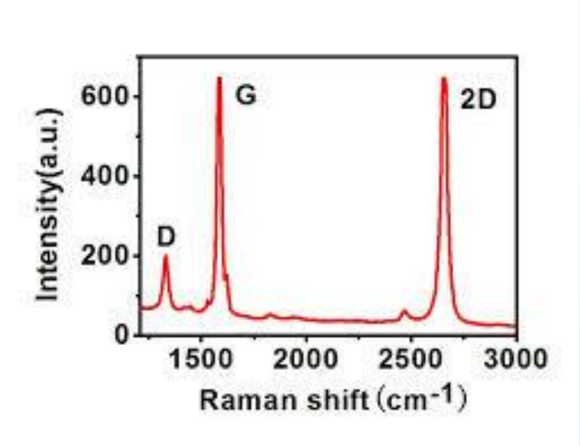


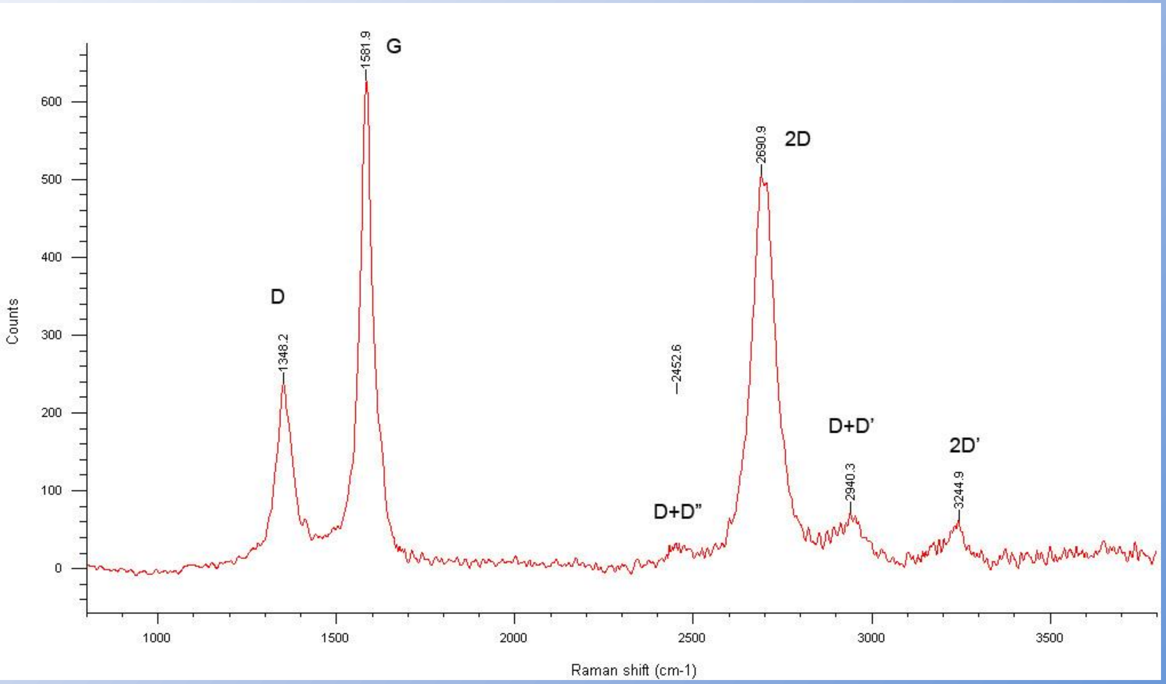
XPS survey scan of a representative graphene sample showing the relative presence of carbon (C1s peak) and oxygen (O1s peak).

- The carbon content of the graphene sheets ranges from 96% to 98.5% while the oxygen content is in the range of 1.4% to 3%.
- In comparison, more widely used chemical reduction methods reduce oxygen content to 10% or higher. Our laser reduction method produces a more pure graphene sample.
- The carbon and oxygen content of the unreduced graphene oxide ranges between 66% to 70% and 29% to 32% respectively.

Results: Raman Spectrum



Ideal Raman spectrum of graphene.



Actual Raman spectrum of a graphene sheet.

- Raman spectrum of the graphene sheet shows the *G*, 2*D*, *D+D"*, and *2D'* bands that are characteristic of graphene, as well as a Raman-forbidden band, *D+D'*, that arises from defects.
- Defects could be edges, functional groups, or structural disorders

Current Energy Storage Technology

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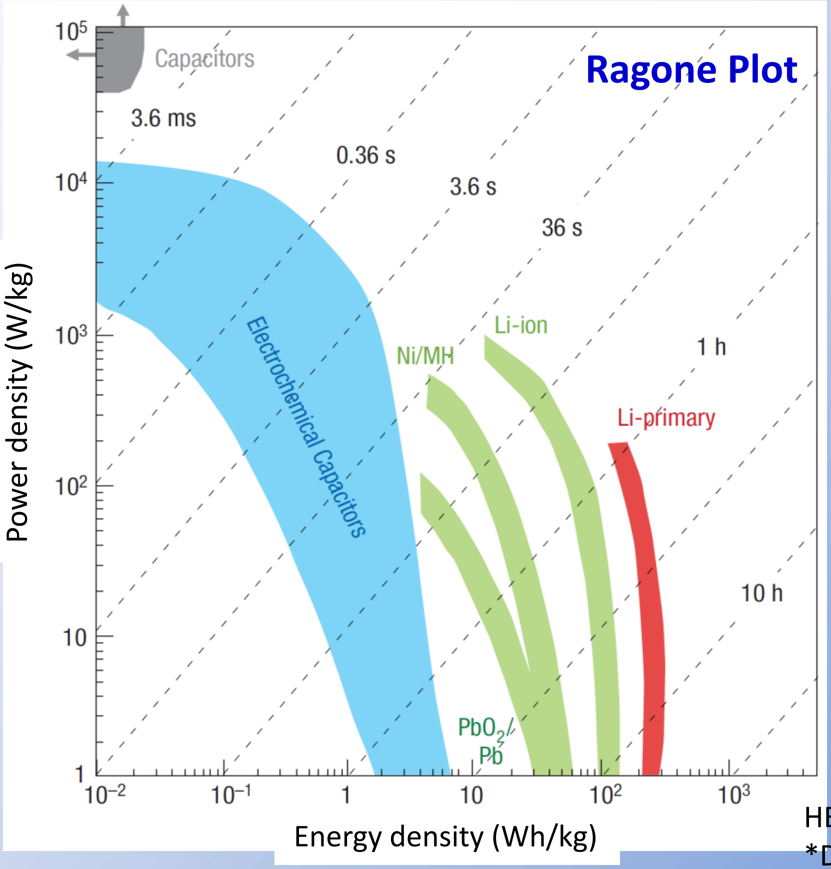
capacitors

supercapacitors



batteries

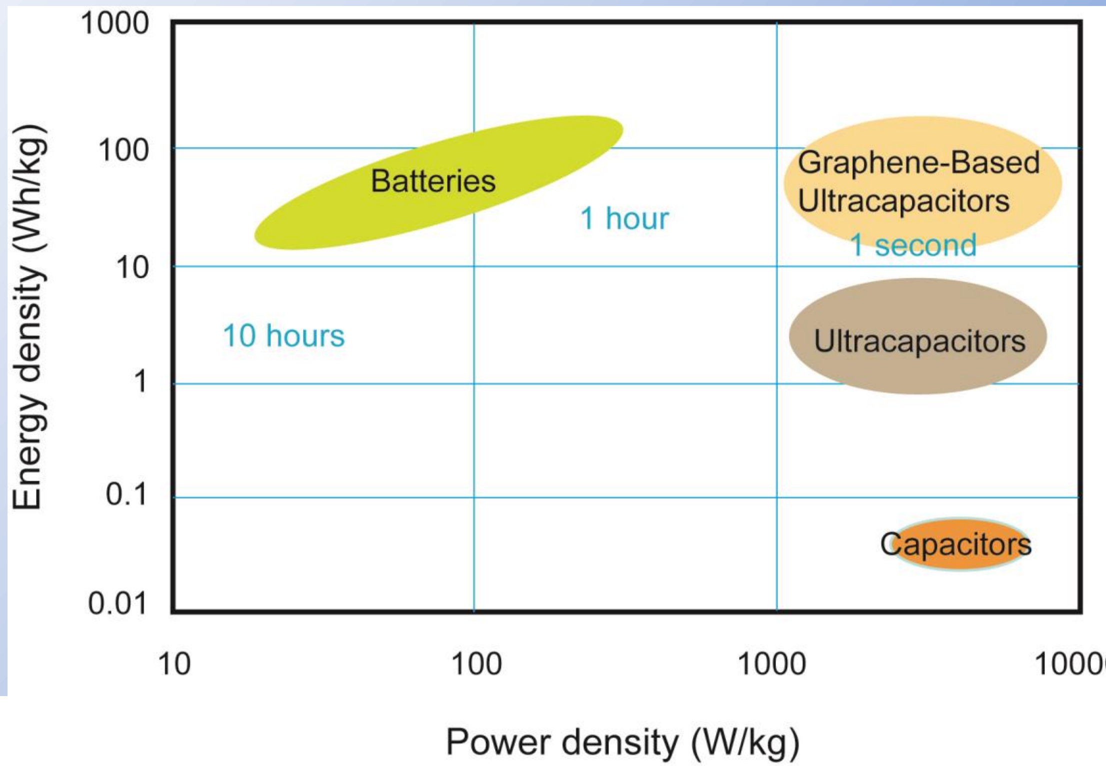
HEV = hybrid electric vehicles
*D. Howell, U.S. Department of Energy, 2008

- **Problem:** Achieving both high energy and high power density
- **Solution:** Electrodes with high surface area and high conductivity

Expected Performance of Graphene devices

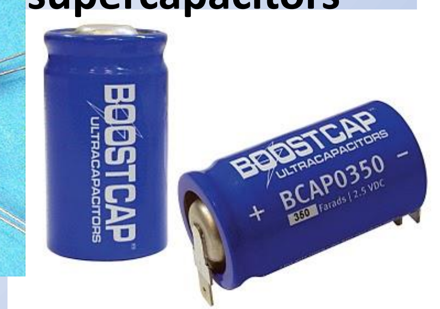
Graphene-based ultracapacitors:

- High power densities
- High energy densities



capacitors

supercapacitors

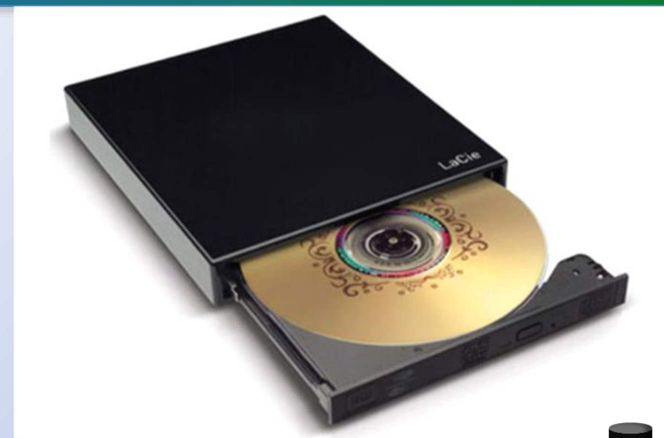


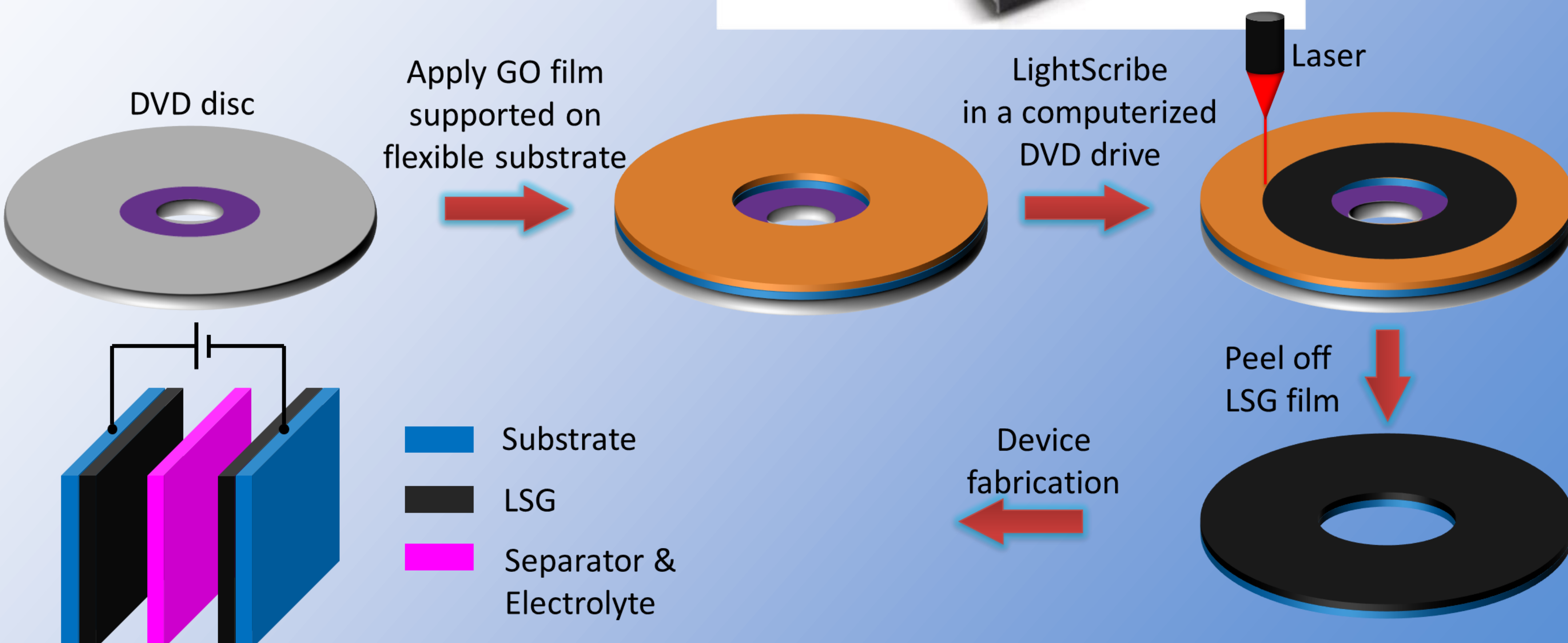
batteries

Energy and power density comparison for batteries, conventional ultracapacitors, and the expected performance of graphene-based ultracapacitors. Charging times are shown in blue.

Making Graphene Supercapacitors in a DVD Burner

Making graphene supercapacitors is as easy as burning a DVD





High-Performance Laser Scribed Graphene Electrodes

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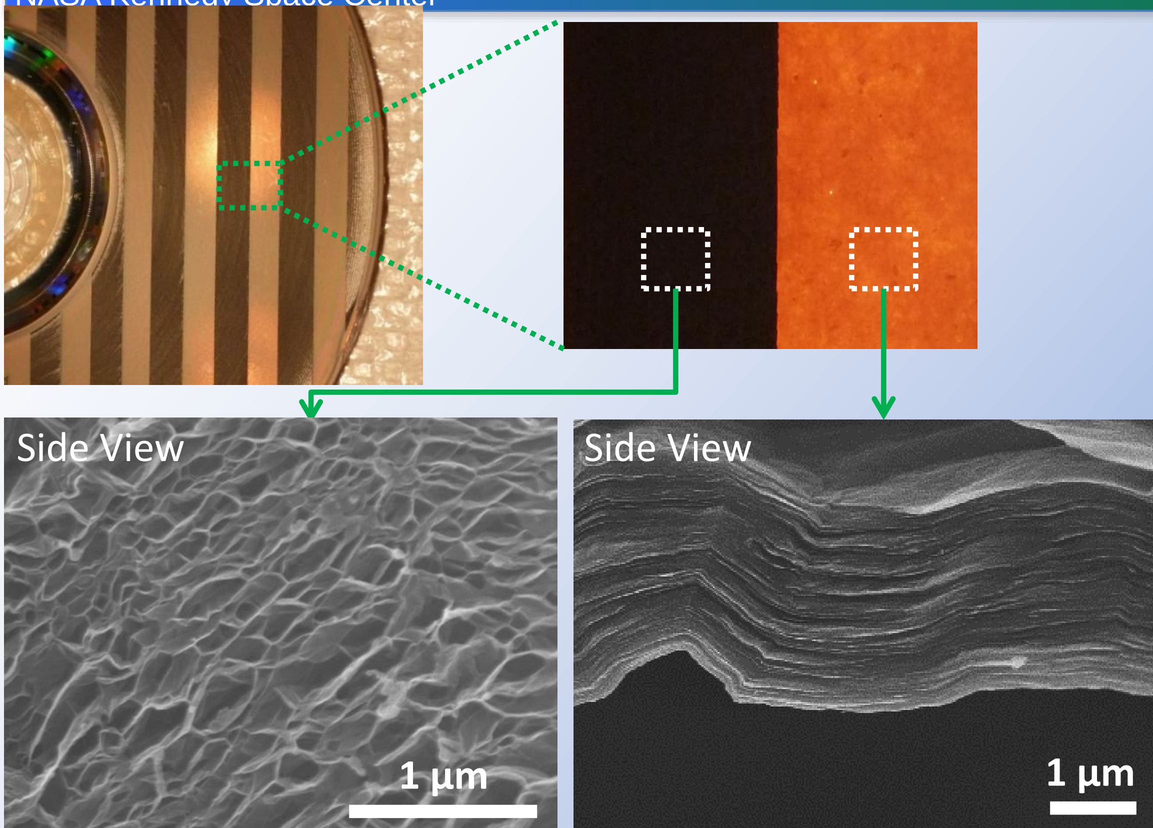

	Activated Carbon	LSG	Impact
Electrical conductivity (S/m)	10-100	1740	High power density
Surface area (m^2/g)	1000-2000 (micropores)	1520 (accessible)	High energy density
Mechanical properties	Powder	Flexible electrodes	Flexible devices
Binders and current collector	Yes	No	Simple fabrication

Need for Flexible Energy Storage

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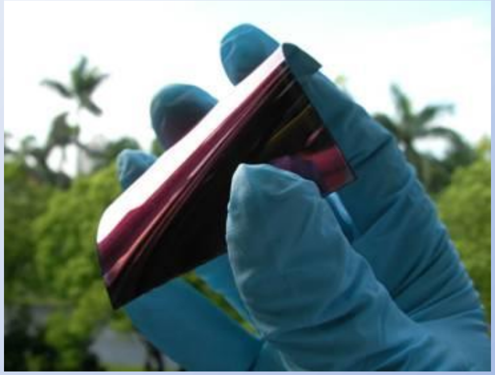
LG Electronic Newspaper

Flexible keyboard

Wearable electronics (*ECG patch)*



Flexible polymer solar cell

Samsung flexible AMOLED display

Flexible, All-Solid State Supercapacitors

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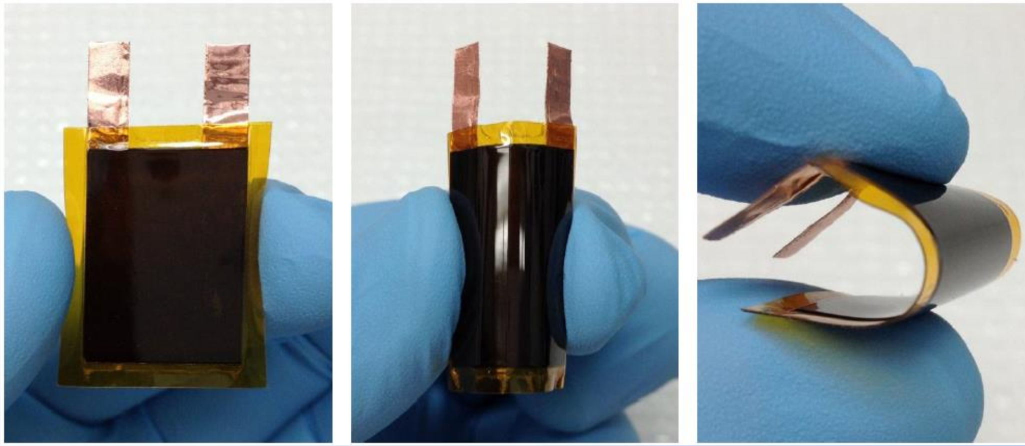

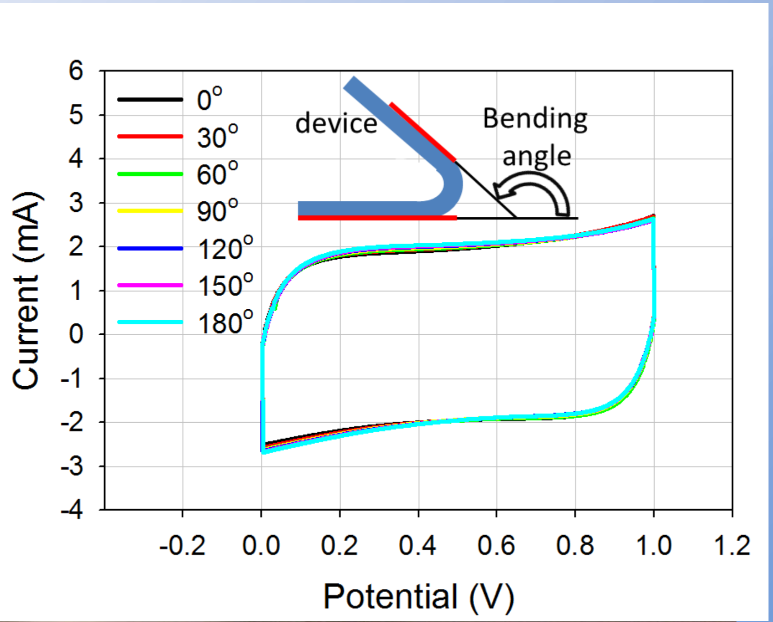

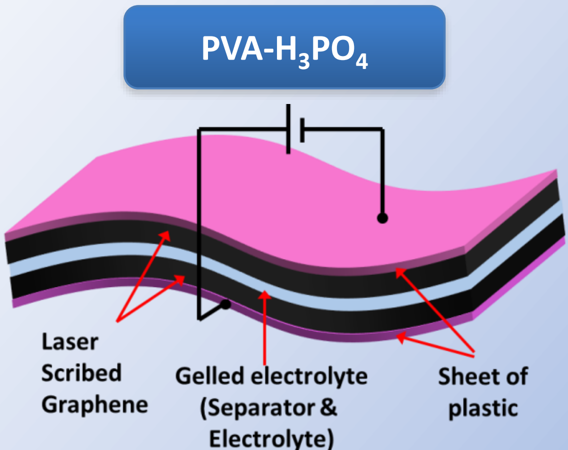

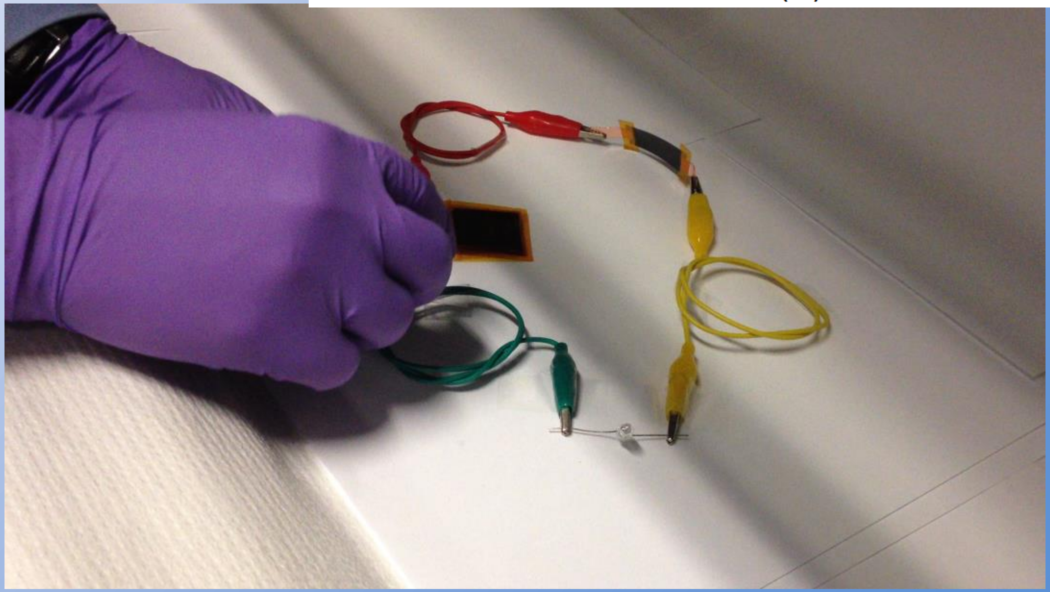

Tandem Supercapacitors

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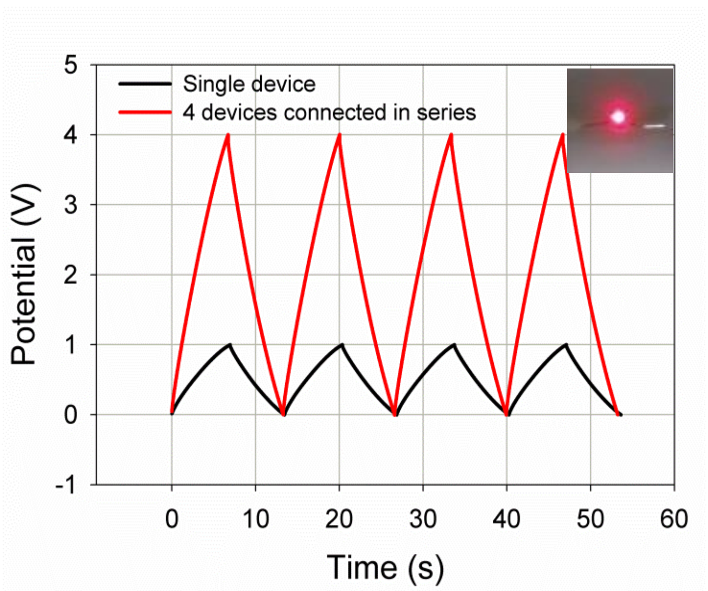
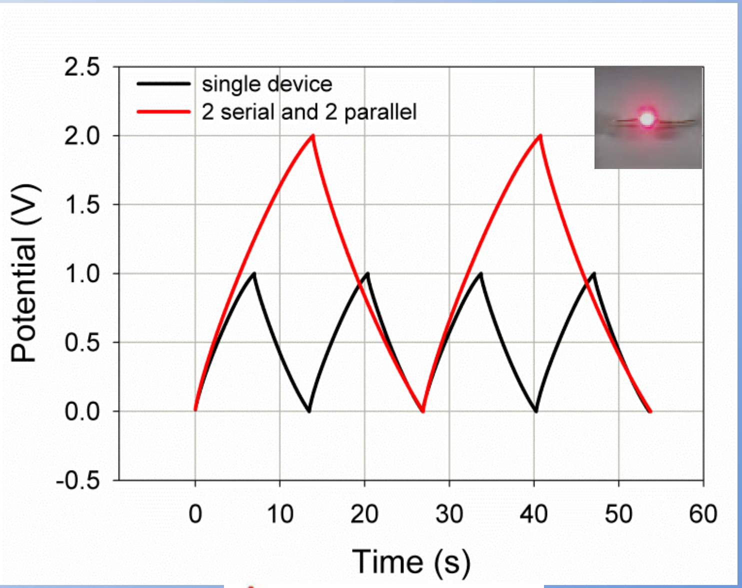
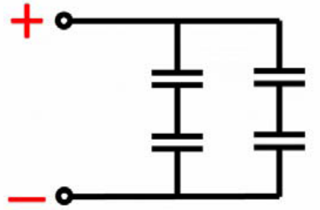
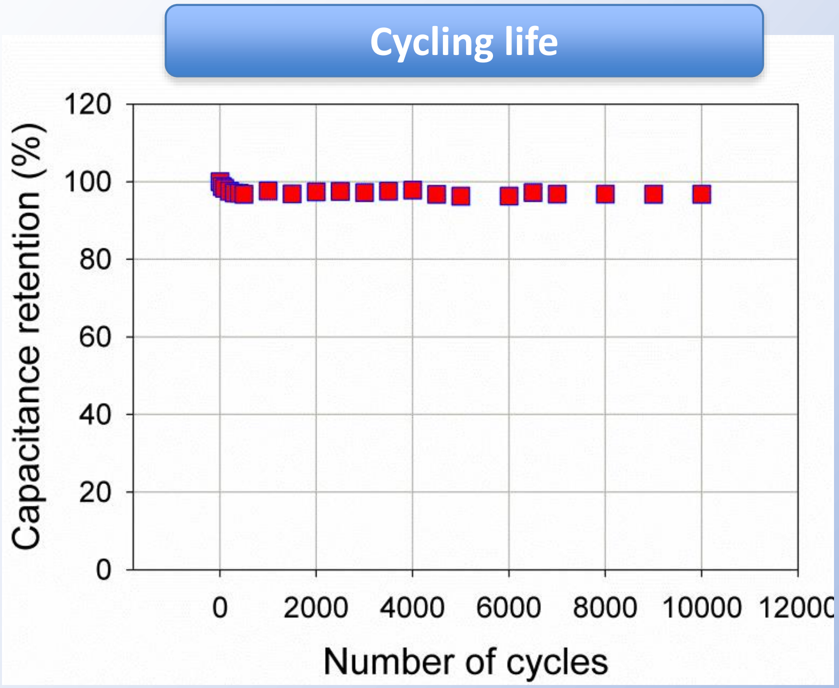
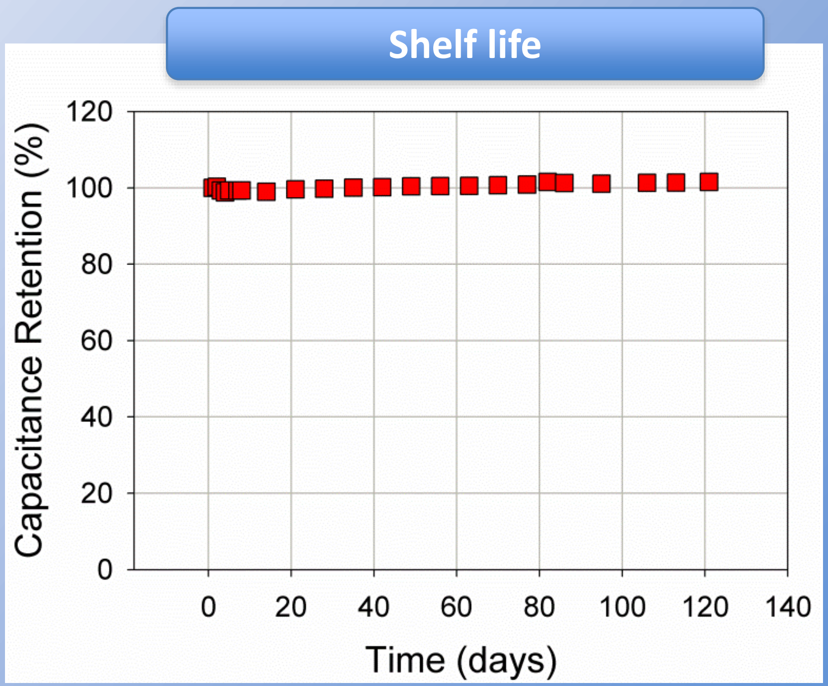






Cycling and Shelf-Life





Slide courtesy of UCLA, Kaner Laboratory

Comparison of LSG, AC, Thin-film Li

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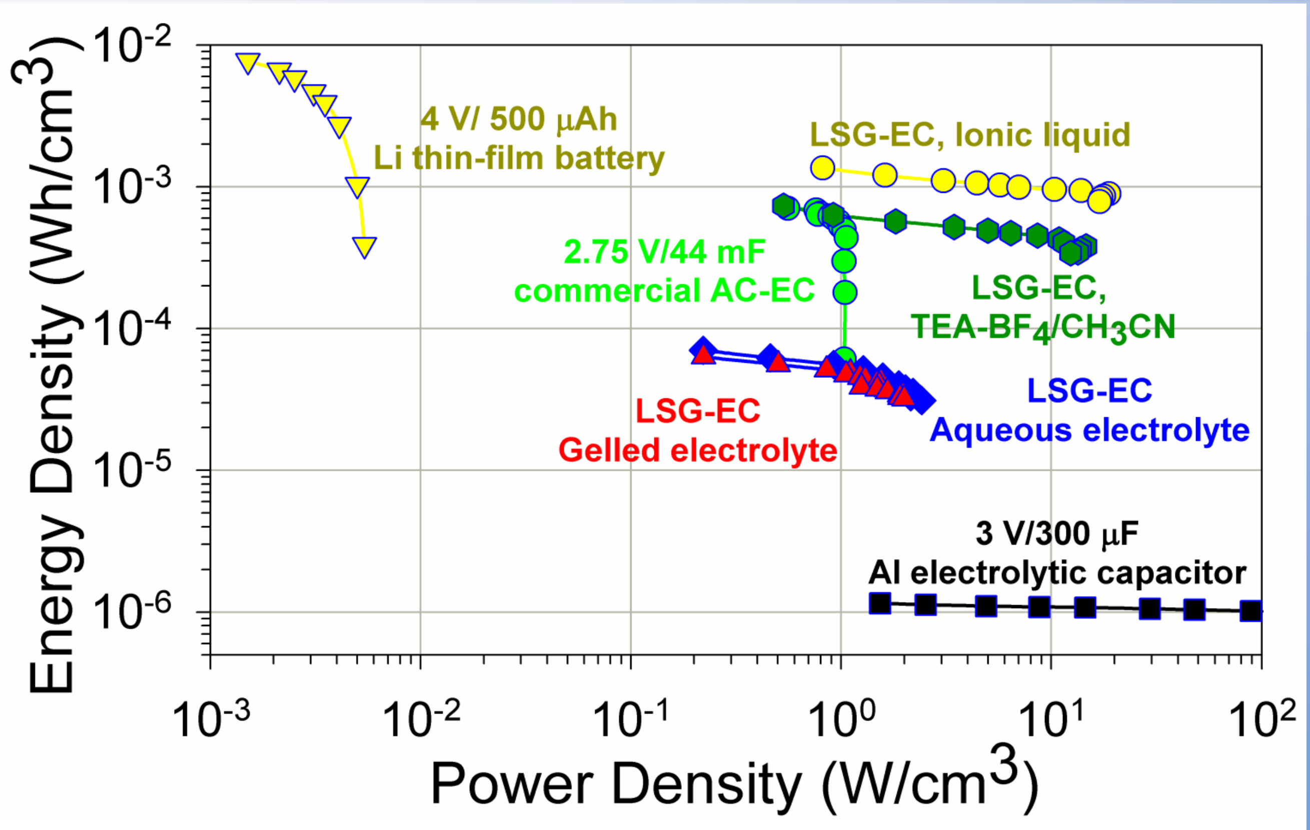

- The plot shows the energy density and power density of the stack for all the devices tested (including current collector, active material, electrolyte and separator).
- Additional features: flexible, lightweight, current collector free and binder free

Slide courtesy of UCLA, Kaner Laboratory

Impact of the Innovation

- Commercial ultracapacitors are currently being used in transportation. A fleet of buses near Shanghai has been running on ultracapacitors for the past several years. Only disadvantage: frequent stops due to low energy densities.
- Graphene-based ultracapacitors promise energy densities greater than existing commercial electrochemical ultracapacitors by an order of magnitude. They also have greater power densities than lithium-ion batteries by an order of magnitude.
- GO, the precursor for the production of graphene, is manufactured on the ton scale at low cost as opposed to lithium, which is a limited resource that must be mined throughout the world.
- A robust, lightweight, flexible, thin, and inexpensive energy storage device with energy and power densities superior to those of state-of-the-art energy storage devices will greatly benefit NASA and the nation's aeronautics.
- Such revolutionary energy storage devices will radically reduce the mass and weight of energy storage and supply devices resulting in more efficient aircraft.

Application to Space

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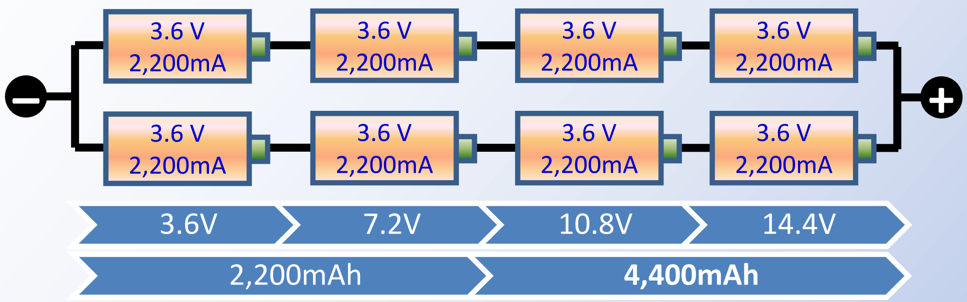
- Higher power density will enable a new class of operations
- Potential for much wider temperature operation: carbon melting point (4900K)
- Increased safety-margin due to reduced fire and toxicity risk
- In-situ resource available from regolith or waste stream

Next Steps



- Increase in voltage produces a substantial increase in the energy density of a supercapacitor ($E = \frac{1}{2}CV^2$)
- Investigate new solvents and electrolytes with higher ion conductivity that would yield voltages suitable for aeronautics applications
- Investigate combinations of these electrolytes for higher performance
- Scale up graphene sheet production with our laser system
- Build prototypes to demonstrate feasibility of graphene-based ultracapacitors for aeronautics applications

III. Filtration Systems

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- Filtration Systems for ISRU:
- Living off the Land: ISRU-Production of
  - mission consumables
  - construction
  - manufacturing and repair
  - Energy and utilities
- Production of oxygen, methane, and water from the Martian atmosphere requires dust removal
- Electrostatic Precipitator capable of working at 1/100 atm

Concept for an oxygen and fuel production plant

Graphene Oxide Filters for Liquids and Gases

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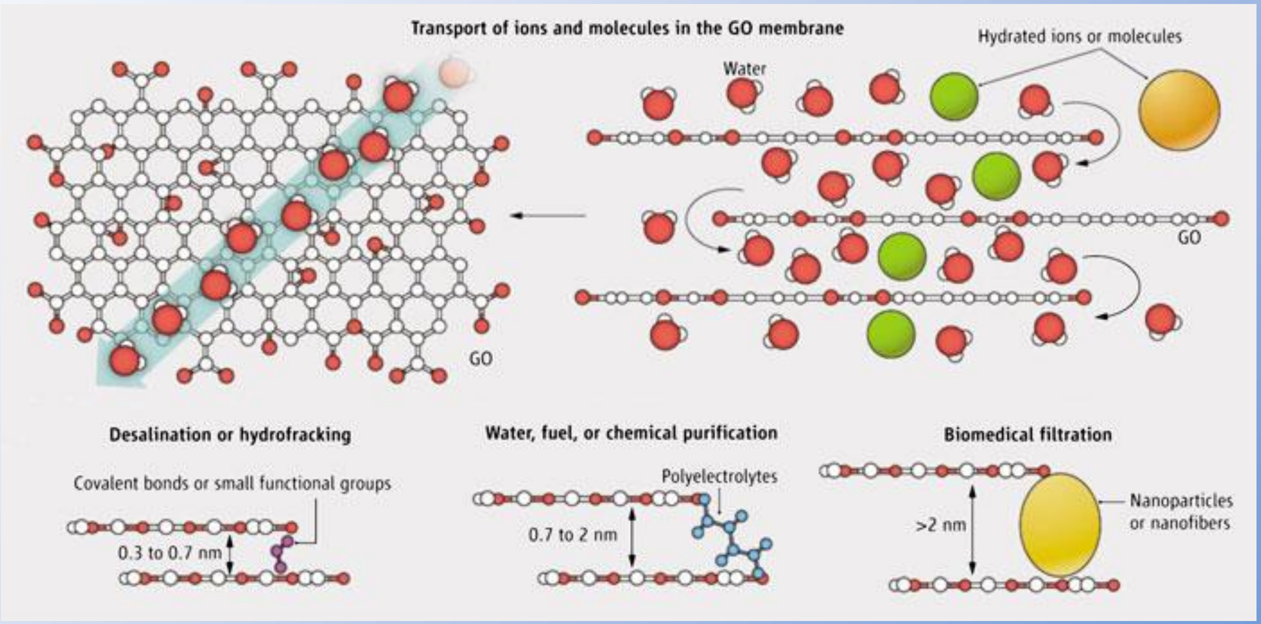
- Andre Geim at the University of Manchester showed that membranes of stacked graphene oxide (GO) sheets are impermeable to all gases and vapors except for water.
- The graphene-oxide sheets are arranged in such a way that there is room for only one layer of water molecules.
- In the absence of water, however, the capillaries shrink and do not let anything through, thus making the material impermeable to everything but water.



Water and small-sized ions and molecules permeate super fast in the graphene-oxide membrane, but larger species are blocked. The size of the membrane mesh can be tuned by adjusting the nanochannel size. (Courtesy: *Science*)

GO Filters for Space

- GO membranes immersed in water block all molecules or ions with a hydrated size larger than 9 Å.
- Ions pass through the membrane 1000 times faster than expected by diffusion
- Capillaries between graphene oxide flakes act as powerful vacuum cleaners
- We are looking at its feasibility for space applications

In Summary

- Graphene offers exciting possibilities for future space applications
- We are taking advantage of its properties to develop technologies for
  - High energy density/Power density energy storage devices that are flexible and safe
  - Filters for space habitats

Acknowledgments

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  Director

  Facultad de Ingeniería y Tecnología

  Universidad Autónoma del Carmen

Thank you!